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The $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ band-systems of OH and OD

By R. F. Barrow[1]

With 2 figures in the text

Abstract

Detailed analysis of the bands discovered by Schüler and Woeldike (*Phys. Z.*, *44*, 435, 1943) confirms the view that they arise from a transition $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ in OH. Values of the constants for the state $B\,^2\Sigma^+$ are:

	T_e	ω_e	B_e	r_e
OH	69775	940	5.54	1.80 Å
OD	69790	684	2.91	

The dissociation energy of the hydroxyl radical, $D_0''(\text{OH})$, is found to be $101.3_3 \pm 0.3$ Kcal. The positions of bands in the expected system B $^2\Sigma^+$–$X\,^2\Pi$ of OH are predicted. Other ultra-violet bands are briefly discussed.

Introduction

Bands discovered by Schüler and Woeldike [1], and studied later by Schüler and Reinebeck [2], Schüler, Reinebeck and Michel [3] and Benoist [4], have recently been shown [5] to arise from a transition $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ in OH and OD. $A\,^2\Sigma^+$ is the upper state of the well-known ultra-violet system, $A\,^2\Sigma^+$–$X\,^2\Pi$. The state $B\,^2\Sigma^+$ correlates with $\text{O}\,(^1D_2) + \text{H}\,(^2S_{1/2})$, and its potential energy-distance curve is very shallow. The bands so far observed correspond to transitions to high vibrational levels of $A\,^2\Sigma^+$, $4 \leq v'' \leq 9$ in OH and $7 \leq v'' \leq 11$ in OD.

Although further experimental work on the B–A bands is still in progress, it seems desirable to give a more detailed account of the analysis, partly because it can be carried somewhat further than was done originally [5], and partly because the results lead to a rather precise value for the energy of dissociation of the hydroxyl radical.

Rotational analysis

The bands consist of simple P and R branches: no spin-doubling has yet been reported. Earlier estimates of the rotational constants in the OH bands [3, 4] suffer from neglect of terms in the centrifugal stretching constants, D, which are important: the analyses of the OD bands [3] are incorrect. In what follows, the measurements were taken from the previous work [3, 4], and where possible mean values were

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[1] Physical Chemistry Laboratory, University of Oxford.

Table 1. Values of $\Delta_2 F_0'(K)$ for OH.

Band . . .	0,5	0,6	0,7	0,5	0,6	0,7	0,8	Calculated value*
Reference .	3	3	3	4	4	4	4	
K 1	31	32			31	31		31.1
2		53			52	50		51.7
3	72	73		78	70		71	72.2
4	92	92		85	90			92.4
5		110		113	112			112.3
6	128	132	133	136	131			131.8
7	154	151	148	150	150	153	149	150.8
8			171	171	167	170	168	169.3
9				185	190	187	178	187.2
10						203	182	204.5
11						220		221.0
12						239		236.8
13						252		251.6

* With $B' = 5.19_3$, $D' = 1._{46} \times 10^{-3}$.

Table 2. Values of $\Delta_2 F_0'(K)$ for OD.

Band . . .	0,7	0,9	0,10	Calculated value
Reference .	3	3	3	
K 1				16.5
2	28			27.4
3	42	39	40	38.3
4	52	51	44	49.2
5	62	54	65	60.0
6	70	65		70.8
7	81	83	78	81.5
8	90	94		92.1
9	106	103	103	102.6
10		113		112.9
11			120	123.2
12		134	128	133.3
13			144	143.2
14		155	154	153.0
15		161	167	162.7
16		167	176	172.1
17			181	181.4
18		187		190.4

* With $B' = 2.74_4$, $D' = 2._5 \times 10^{-4}$.

derived from the two sets of measurements, after taking account of a small, apparently systematic, shift between them.

The rotational constants for the lowest vibrational level of $B\,^2\Sigma^+$ were first derived by taking mean values for all the available combination differences, $\Delta_2 F'(K)$: the

Table 3.

The B–A system of OH

$B_0' = 5.19_5,\ D_0' = 1._5 \times 10^{-3}$
$B_1' = 4.20,\ D_1' = 2 \times 10^{-3}$

v', v''	ν_0	B''	D''
0,5	23 044	12.62	$2._4 \times 10^{-3}$
0,6	21 126	11.54	$3._1$
0,7	19 501	10.20	$4._1$
0,8	18 227	8.4_6	5
1,5	23 701		
1,6	21 787		

The B–A system of OD

$B_0' = 2.74_4,\ D_0' = 2._5 \times 10^{-4}$

v', v''	ν_0	B''	D''
0,7	23 014	6.68_5	$7._7 \times 10^{-4}$
0,9	20 303	5.79	$8._5$
0,10	19 186	5.22_5	10

Table 4. The 0,9 band of OD.

K	$R_{\text{obs.}}$	$R_{\text{calc.}}$	$P_{\text{obs.}}$	$P_{\text{calc.}}$
0	20 310*	20 308.7		
1	307*	308.1		20 291.6
2	299	301.4	20 274*	274.0
3	287	288.6	248	250.3
4	270	269.8	219	220.6
5	241	245.2	187	185.2
6	213	214.4	148	143.7
7	180	178.0	097	096.6
8	137	135.8	043	043.7
9	089	088.0	19 986	19 985.4
10	034	034.7	921	921.8
11	19 976*	19 975.9	852	852.8
12	913	912.0	779	778.8
13	843	843.3	699*	700.0
14	769	769.4	614	616.3
15	691	691.0	530	528.4
16	606	608.0	439	436.0
17	522	520.9	341*	339.6
18	431	429.7	244*	239.3

* Overlapped.

constants B_0' and D_0' were then obtained by plotting $\Delta_2 F'(K)/(K+\frac{1}{2})$ against $(K+\frac{1}{2})^2$ in the usual way. Values of the combination differences are given in Tables 1 and 2.

The positions of the band-origins, ν_0, and of the lower-state constants were then derived using

$$R(K-1)+P(K)=2\,\nu_0+2(B'-B'')K^2-2(D'-D'')K^2(K^2+1).$$

Estimates of B_1' for OH were made from the 1,5 and 1,6 bands [4]. For the 1,5 band, $2\Delta B$ ($=2(B''-B')$) was found to be 16.89_4, and from the 1,6 band, $2\Delta B = 14.63_5$. With the values of B'' given in Table 3, $B_1' = 4.18_0$ and 4.22_2 respectively. We take the mean value, $B_1' = 4.20$ cm^{-1}.

The constants obtained are given in Table 3. The extent to which they are successful in reproducing the measurements is illustrated in Table 4, where observed and calculated positions of lines are given for the 0,7 band of OD.

The $A\,^2\Sigma^+$ *states*

The way in which the rotational constants, B_v, and the vibrational intervals, $\Delta G_{v+1/2}$, vary with vibrational quantum number is illustrated in Fig. 1. The fact that the new values of the constants fit so well with the well-established values for the lower vibrational levels of the $A\,^2\Sigma^+$ states is strong evidence for the present interpretation of the bands.

The values of the rotational constants for the $A\,^2\Sigma^+$ states are collected in Table 5. It is likely that a large number of terms would be required in equations derived to reproduce the values of B_v exactly, and no effort has been made to do this. The fit

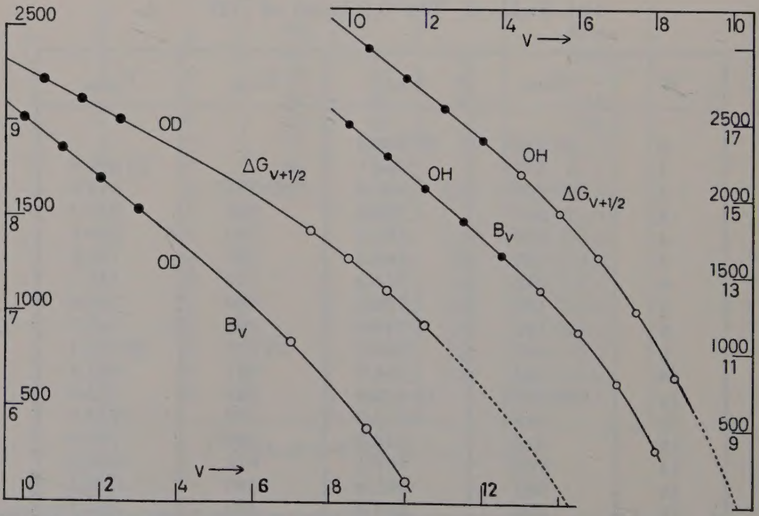

Fig. 1. ΔG_v and B_v plotted against v for the $A\,^2\Sigma^+$ states of OH (right-hand scales) and OD (left-hand scales).

● – – – points from $A\,^2\Sigma^+$–$X\,^2\Pi$ systems,
○ – – – points from $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ systems.

Table 5. Rotational constants for the $A\,^2\Sigma^+$ states of OH and OD.

v	OH			OD	
	$B_{\text{obs.}}$	$B_{\text{calc.}}$ *	$D_{\text{obs.}}$	$B_{\text{obs.}}$	$D_{\text{obs.}}$
0	16.961	16.961	2.04×10^{-3}	9.036_9	$5.5_5 \times 10^{-4}$
1	16.129	16.142	2.03	8.714	5.4_6
2	15.287	15.291	2.08	8.393	5.5_2
3	14.422	14.408	2.06	8.068	5.5_1
4	13.494	13.493	2.0_5	(7.74)†	
5	12.62	12.55	$2._4$	(7.40)	
6	11.54	11.57	$3._1$	(7.05)	
7	10.20	10.56	$4._1$	6.68_5	$7._5$
8	8.4_6	9.51	5	(6.26)	
9				5.79	$8._5$
10				5.22_5	10

* From $B_v = 17.358 - 0.786_8(v + \frac{1}{2}) - 0.016\,(v + \frac{1}{2})^2$, which was derived to fit B_v from $v = 0$ to $v = 4$.

† The values in parentheses are interpolated estimates.

Table 6. Vibrational intervals and term-values for the $A\,^2\Sigma^+$ states of OH and OD.

v	OH		OD		v	OH	OD
	$\Delta G_{\text{obs.}}$	$\Delta G_{\text{calc.}}$	$\Delta G_{\text{obs.}}$	$\Delta G_{\text{calc.}}$		G_v	G_v
0.5	2 988.55[a]	2 988.55	2 214.6[e]	2 214.6	0	1 566.0	1 147.6
1.5	$2\,793.0_2$[a]	2 793.0	2 111.5[e]	2 110.3	1	4 554.6	3 362.2
2.5	$2\,593.5_4$[a]	2 593.1	$2\,007._5$[e]	2 007.5	2	7 347.6	5 472.4
3.5	2 385.5[b]	2 385.9	–	$1\,903.8_5$	3	9 440.7	7 479.9
4.5	2 162[c]	$2\,164.0_5$	–	1 796.8	4	12 326.6	9 383.8
5.5	1 918[d]	1 916.0	–	1 683.8	5	14 490.6	11 180.6
6.5	1 625[d]	$1\,625.7_5$	–	1 562.0	6	16 406.6	12 864.4
7.5	1 274[d]	1 273.2	1 426[f]	1 428.8	7	18 032.3	14 426.4
8.5	844[c]	834	1 280[f]	1 281.3	8	19 305.6	15 855.2
9.5		279	1 117[d]	1 116.6	9	20 140	17 136.5
10.5			932[f]	931.6	10	20 418	18 253.2
11.5				723	11		19 185
12.5				488	12		19 908
13.5				224	13		20 396
					14		20 620

[a] Calculated from data of Dieke and Crosswhite [6].

[b] Calculated from data of Tanaka and Koana [7].

[c] Private communication from Professor Schüler [17].

[d] From Table 3.

[e] Calculated from data given in references [8–11].

[f] From reference [3].

[g] Values of ΔG for OD calculated from equation (2) for OH, using the isotope relations, are 2213.9, 2111.2, 2006.9, 1429.0, 1285.4, 1117.9 and 925.8 cm^{-1}.

of the values of B_v for OH derived from the $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ bands with those from the $A\,^2\Sigma^+$–$X\,^2\Pi$ system may, however, be seen from the figures in Table 5. The calculated values of B_v given here are from

$$B_v = 17.358 - 0.786_8\,(v + \tfrac{1}{2}) - 0.016\,(v + \tfrac{1}{2})^2,$$

which was derived to reproduce as well as possible the values of B_v from $v = 0$ to $v = 4$. The extrapolated values for $v = 5$, 6 and 7 are in as good agreement with the observed values of B_v from the $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ bands as could be expected.

Equations which give *approximate* fit over the whole range of observed values are:

$$\begin{aligned} \text{OH:}\quad B_v &= 17.384 - 0.839_2\,(v + \tfrac{1}{2}) - 3.7 \times 10^{-5}(v + \tfrac{1}{2})^5 \\ \text{OD:}\quad B_v &= 9.198 - 0.322_4\,(v + \tfrac{1}{2}) - 4.5 \times 10^{-6}(v + \tfrac{1}{2})^5. \end{aligned}$$

Values of the vibrational intervals in $A\,^2\Sigma^+$ are given in Table 6. Meinel [12] has already drawn attention to the difficulty of reproducing the observed vibrational intervals in the ground state of OH, and likewise the intervals in the $A\,^2\Sigma^+$ states follow no simple relations. Equations have been calculated in two ways. First, values of $y_e\omega_e$ and of $z_e\omega_e$ were derived from the intervals in OH and OD, and thence mean values of these constants were derived, assuming that the isotope relations hold good. Values of ω_e and of $x_e\omega_e$ were then derived in the usual way. The expressions are:

$$\begin{aligned} \text{OH:}\quad G_v &= 3203.2_8(v + \tfrac{1}{2}) - 113.8_5(v + \tfrac{1}{2})^2 + 4.59\,(v + \tfrac{1}{2})^3 - 0.48\,(v + \tfrac{1}{2})^4 \\ \text{OD:}\quad G_v &= 2335.0_5(v + \tfrac{1}{2}) - 60.4_8(v + \tfrac{1}{2})^2 + 1.77\,(v + \tfrac{1}{2})^3 - 0.13_5(v + \tfrac{1}{2})^4. \end{aligned} \tag{1}$$

The isotope relations are fulfilled quite accurately by the constants ω_e and $x_e\omega_e$: thus

$$\begin{aligned} (\omega_e)_{\mathrm{OH}}/(\omega_e)_{\mathrm{OD}} &= 1.371_8 \text{ (calc: 1.3736)} \\ (x_e\omega_e)_{\mathrm{OH}}/(x_e\omega_e)_{\mathrm{OD}} &= 1.882_5 \text{ (calc: 1.8868).} \end{aligned}$$

These expressions, however, fail to reproduce exactly the values of ΔG at low values of v.

For the present purpose, which is to calculate the dissociation limit in the $A\,^2\Sigma^+$ states, it was decided to determine independent empirical equations to represent the observed intervals in OH and OD as closely as possible. We obtain

$$\begin{aligned} \text{OH:}\quad G_v &= 3178.8_6(v + \tfrac{1}{2}) - 92.91_7(v + \tfrac{1}{2})^2 - 1.791_5(v + \tfrac{1}{2})^3 + 0.3236_2(v + \tfrac{1}{2})^4 - \\ &\qquad - 0.03585\,(v + \tfrac{1}{2})^5 \\ \text{OD:}\quad G_v &= 2322.6\,(v + \tfrac{1}{2}) - 55.4_5(v + \tfrac{1}{2})^2 + 1.0365\,(v + \tfrac{1}{2})^3 - 0.09333\,(v + \tfrac{1}{2})^4 - \\ &\qquad - 6.78 \times 10^{-4}(v + \tfrac{1}{2})^5. \end{aligned} \tag{2}$$

The equations (2) reproduce the observed values of ΔG_v very closely (Table 6). The coefficients in (2) clearly do not fulfill the isotope relations, but this failure is not in fact significant: for the expression for G_v(OD) derived from equation (2) for OH by division of the coefficients by the appropriate power of ϱ gives agreement with the experimental intervals which is very nearly as satisfactory as is given by the independent equation (2) above (see Table 6).

The $B\,^2\Sigma^+$ states

It became clear at an early stage of the analysis that it is most probable that the lowest observed vibrational levels in the upper states have $v' = 0$. For if this were not the case, one would expect to find stronger bands at shorter wavelengths. We may assume then that the vibrational intervals [3] of 660 cm^{-1} in OH, and of 546 and 360 in OD represent $\Delta G_{1/2}$, and $\Delta G_{1/2}$ and $\Delta G_{3/2}$ respectively. The vibrational levels in the $B\,^2\Sigma^+$ states probably depart very considerably from those of a simple harmonic oscillator: the best that we can do is to assume that they follow a three-constant expression

$$G_v = \omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 - y_e\omega_e(v+\tfrac{1}{2})^3.$$

If we further make use of the isotope relations between the constants, we may proceed to derive

$$\begin{aligned}\text{OH:}\quad & G_v = 939._{95}(v+\tfrac{1}{2}) - 105.0_4(v+\tfrac{1}{2})^2 - 21.5(v+\tfrac{1}{2})^3\\ \text{OD:}\quad & G_v = 684.3(v+\tfrac{1}{2}) - 55.6_7(v+\tfrac{1}{2})^2 - 8.2_{95}(v+\tfrac{1}{2})^3.\end{aligned}$$

These equations lead to the following vibrational term-values:

	OH		OD
G_0	441.0	G_0	327.3
G_1	1 101.0	G_1	873.2
$G_2 \simeq G_{\max} =$	1 357.5	G_2	1 233.3
		$G_3 \simeq G_{\max} =$	1 357.5

The estimation of the equilibrium rotational constants presents some difficulty. In the end, a value of α_e for OH was obtained by trial and error from the Pekeris relation

$$\alpha = 6/\omega_e\,[(x_e\,\omega_e\,B_e^3)^{\frac{1}{2}} - B_e^2]:$$

γ was then derived from the difference between B_0 and B_1 for OH, and values of α and γ for OD were calculated using the isotope relations. We then obtain:

$$\begin{aligned}\text{OH:}\quad & B_v = 5.54 - 0.65_3\,(v+\tfrac{1}{2}) - 0.16\,(v+\tfrac{1}{2})^2.\\ \text{OD:}\quad & B_v = 2.91 - 0.25_2\,(v+\tfrac{1}{2}) - 0.04_5\,(v+\tfrac{1}{2})^2.\end{aligned}$$

It is difficult to assess the reliability of these estimates of B_e. However, they satisfy approximately the isotope relations, giving $r_e = 1.80$ Å, and they fit the observed values of B reasonably closely, thus

		$B_{\text{obs.}}$	$B_{\text{calc.}}$
OH	$v=0$	5.19	5.17
	$v=1$	4.20	4.20
OD	$v=0$	2.74	2.77

Electronic energy of the states $B\,^2\Sigma^+$ and the dissociation energy of OH *and* OD

The values of $\nu_{0,0}$ for the A–X systems, as calculated with the relations of Almy and Horsfall [13] are 32402.3 and $32477._4$ cm^{-1} for OH and OD respectively. Using the constants given by Herzberg [14] for the ground states X, and the values of G_0 for the states A given in Table 6, we obtain $\nu_e = 32683._2$ and $32679._2$ cm^{-1} for OH and OD respectively. The values of T_0 for $B\,^2\Sigma^+$ are 68369 and 68768 cm^{-1} for OH and OD respectively: the corresponding values of ν_e are 69775 and 69790 cm^{-1}.

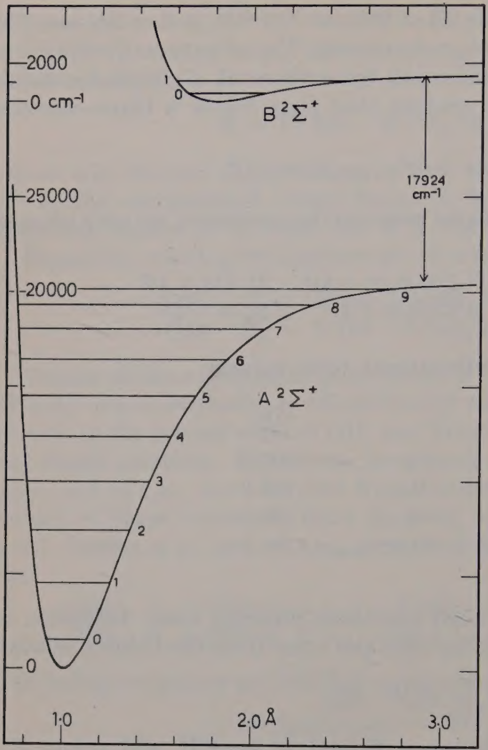

Fig. 2. Potential energy curves for the $A\,^2\Sigma^+$ and $B\,^2\Sigma^+$ states of OH and OD. The vibrational levels are for OH.

Considering the uncertainties in the values of G_0 for the B-states, the agreement between the two estimates of T_e may be regarded as satisfactory.

We now consider the energy of dissociation. Observations on the thermal dissociation of of water vapour [15] lead [16] to $D''(\mathrm{OH}) = 100.2 \pm 0.9$ Kcal, or 35054 ± 315 cm^{-1}. The excitation energies of $\mathrm{O}(^1D)$ and of $\mathrm{O}(^1S)$ above $O(^3P)$ are 15868 and 33792 cm^{-1}, and since there are no other low-lying atomic states, the $A\,^2\Sigma^+$ states must correlate with $O(^1D) + H$, and the $B\,^2\Sigma^+$ states with $O(^1S) + H$. (The correlation of the lower state of the Schüler bands with $O(^1D)$ and of the upper state with $O(^1S)$ has already been pointed out by Benoist [4].) We have then the following estimates for D_0'' (referred to the level $J = 1\frac{1}{2}$ in $^2\Pi_{3/2}$ of OH),

	cm^{-1}
From equation (1), $A\,^2\Sigma^+$	35 581
From equation (2), $A\,^2\Sigma^+$: OH	35 427
From equation (2), $A\,^2\Sigma^+$: OD	35 633
$B\,^2\Sigma^+$	35 539

All the values lie within the range 35530 ± 110 cm^{-1} or $101.5_6 \pm 0.3_1$ Kcal. The best guess is that the figure from $A\,^2\Sigma^+$ of OH, where the extrapolation is only about 280 cm^{-1}, is most nearly correct. Equation (2) for this state gives a slightly low value for $\Delta G_{8\,1/2}$, and we may estimate D_0'' a little above 35427 cm^{-1}, say at 35450 cm^{-1}, or 101.3_3 Kcal. It seems unlikely that the error is more than 100 cm^{-1}, and we conclude $D_0''(\mathrm{OH}) = 101.3_3 \pm 0.3$ Kcal.

Potential energy relations

Morse functions for the states A and B are illustrated in Fig. 2. It is very clear from the relative disposition of the two curves that transitions from B only to rather high vibrational levels in A are to be expected, and it is just these transitions that are in fact observed. Little, if any, extension of the systems to shorter wavelengths is to be expected.[1] At longer wavelengths, it is possible that the 0,9 band of OH at about 17360 cm^{-1}, and the 0,12 and 0,13 bands of OD at 17545 and 17070 cm^{-1}, respectively, may be observable.[1]

Discussion: Ultra-violet bands

Benoist [4] and Schüler and Michel [17] have observed bands in the ultra-violet region in discharges which give simultaneously the $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ system. Benoist measured heads at 42120, 40570 and 39300 cm^{-1}, and suggested that they are respectively the 5,1, 6,2 and 7,3 bands of the $A\,^2\Sigma^+$–$X\,^2\Pi$ system of OH. The calculated positions of ν_0 for these bands are 41746, 40270 and 38654 cm^{-1}, so that this suggestion cannot be correct. Schüler and Michel have very recently measured bands at $\nu = 44458$, 42832, 40557 and 39275 cm^{-1}. These bands are degraded to longer wavelengths, and the latter three bands have, under low resolving power, a structure similar to those of the B–A system. The results of rotational analyses of the three bands at longer wavelengths are taken by Schüler and Michel to indicate that they have lower states in common with those of the B–A system. This suggestion raises difficulties which we may now briefly consider.

The evidence that the visible bands represent a transition $B\,^2\Sigma^+$–$A\,^2\Sigma^+$ in OH and OD has been given above. The significant points are:

(I) The vibrational intervals in the lower states of the visible bands have approximately the values that they must take for the dissociation limits of the $A\,^2\Sigma^+$ states to agree with the well-established equilibrium value for the dissociation energy of OH.

(II) The difference between the dissociation limits of the A and B states is very close to the difference in energy $\mathrm{O}(^1S) - \mathrm{O}(^1D)$.

(III) The rotational constants for the lower states of the visible bands fit well with the values extrapolated from $A\,^2\Sigma^+$.

(IV) The isotope relations in the constants for the B states are fulfilled, as far as can be determined from the present data.

(V) The intensities in the visible bands fit reasonably with the view that the transition is from a state B to $A\,^2\Sigma^+$.

(VI) Finally the combination $\mathrm{H}(^2S) + \mathrm{O}((2p^4 \cdot {}^1S_0)$ gives only one molecular state, $^2\Sigma^+$. Thus state B is identified as $B\,^2\Sigma^+$.

The suggestion that the lower states of the ultra-violet bands have lower states in common with those of the visible bands is difficult to accept, for it would indicate that there are still further stable excited states of OH capable of combining with $A\,^2\Sigma^+$, and of giving rise to ultra-violet systems. Examination of the atomic states shows that none are expected (see also Mulliken and Christy [18], Leach [19]).

It is, however, perhaps not impossible that the ultra-violet bands, if they do arise from OH, may be interpreted as follows. Examination of the measurements of Schüler and Michel show rather that they may have their *upper* states in common with $B\,^2\Sigma^+$. If this is so, we are concerned with a transition from $B\,^2\Sigma^+$ to a new state, *a*. Such a state would necessarily correlate with the ground state atoms, $O(^3P) + H$. In addition to the ground state, $^2\Pi$, the ground-state atoms also give $^4\Pi$, $^2\Sigma^-$ and $^4\Sigma^-$ states. These states are not expected to be stable, but if the upper state of the ultra-violet bands is $B\,^2\Sigma^+$, the only likely transition to give bands with only *P* and *R* branches seems to be the forbidden, magnetic dipole transition [14], $B\,^2\Sigma^+$–$a\,^4\Sigma^-$.

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[1] After this had been written, Professor Schüler informed me (11.4. 1956) that he has now observed bands of OH at 25 872 and 18 054 cm^{-1}: these are just in the positions expected for the 1,4 and 1,9 bands, respectively.

The existence of bands of a system $B\,^2\Sigma^+$–$X\,^2\Pi$ in the ultra-violet region is also to be expected. A rough estimate, band on a Morse potential function for the ground state, together with that given in Fig. 2 for $B\,^2\Sigma^+$, and the vibrational energies by Meinel [12], shows that the strongest bands of the $v' = 0$ progression are likely to have $v'' \geq 8$. Values of ν_0 for the 0,8, 0,9 and 0,10 bands are about 44420, 42185 and 40115 cm^{-1} respectively.

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